

## CLAIMS

What is claimed is.

1. An electroplating composition comprising:  
copper;  
at least one acid, selected from sulfuric, methane sulfonic, amidosulfuric,  
aminoacetic, fluoboric, and mixtures thereof;  
at least one halogen;  
at least one additive, selected from an accelerating agent, a suppressing agent, and  
an accelerating-suppressing agent; and  
the solution and mixture products thereof.

2. The aqueous electroplating composition according to claim 1, wherein the at least  
one additive consists of an accelerating agent and a suppressing agent.

3. The aqueous electroplating composition according to claim 1, wherein the at least  
one additive consists of an accelerating agent and an accelerating-suppressing agent.

4. The aqueous electroplating composition according to claim 1, wherein the at least  
one additive consists of a suppressing agent and an accelerating-suppressing agent.

1 5. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent is selected from a disulfide organic compound, a monosulfide organic  
3 compound, and mixtures thereof.

1 6. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent is provided in a concentration range from about 2 micromole/liter to about 500  
3 micromole/liter.

1 7. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent comprises 1-propane sulfonic acid, and 3,3'-dithio-bis di-sodium salt.

1 8. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent comprises 1-propane sulfonic acid, 3-[(ethoxy-thiomethyl)thio], - potassium  
3 salt..

1 9. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent comprises (O-Ethylthiocarbonato)-S-(3-sulfopropyl)-ester, potassium salt.

1 10. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent comprises a phosphonated disulfide.

1 11. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent is selected from a sulphonated monosulfide and a phosphonated monosulfide.

1 12. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating agent is selected from 3-mercapto-1-propanesulfonic acid and 2-  
3 mercaptoethanesulfonic acid sodium salt.

1 13. The aqueous electroplating composition according to claim 1, wherein the  
2 suppressing agent is provided in a concentration range from about 0.6 micromole/liter to about  
3 600 micromole/liter.

1 14. The aqueous electroplating composition according to claim 1, wherein the  
2 suppressing agent is selected from at least one of a polyether, polyethylene glycol, polypropylene  
3 glycol, polyoxyethylene lauryl ether, polyethynene oxide, alkoxyated beta-naphtol, alkyl  
4 naphthalene sulphonate, polyimines, poly amines, and polyamids.

1 15. The aqueous electroplating composition according to claim 1, wherein the  
2 suppressing agent comprises a beta-naphtol having the structure:  
3



5 wherein n may be equal to 1 and wherein m may be equal to 1, and wherein the  
6 molecular weight is in the range from about 800 to about 1,500.

1 16. The aqueous electroplating composition according to claim 1, wherein the  
2 suppressing agent comprises a cross-linked polyamide in a concentration range from about 0.6

3  $\mu\text{mole/liter}$  to about 600  $\mu\text{mole/liter}$ , and wherein the cross-linked polyamide has an average  
4 molecular weight in a range from about 2,000 to about 3,000 gram/mole.

1 17. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating-suppressing agent is provided in a concentration range from about 1  $\mu\text{mole/liter}$  to  
3 about 500  $\mu\text{mole/liter}$ .

1 18. The aqueous electroplating composition according to claim 1, wherein the  
2 accelerating-suppressing agent comprises 1-propanesulfonic acid, 3-[[dimethylamino)-  
3 thioxomethyl]- sodium salt..

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1 19. A method of plating comprising:  
2 providing aqueous electroplating composition, comprising:  
3 copper;  
4 at least one acid, selected from sulfuric, methane sulfonic, amidosulfuric,  
5 aminoacetic, fluoboric, and mixtures thereof;  
6 at least one halogen ion;  
7 at least one additive, selected from an accelerating agent, a suppressing  
8 agent, and an suppressing-accelerating agent; and  
9 the solution and mixture products thereof  
10 contacting a substrate with the plating composition; and  
11 impressing a multi-step direct-current waveform potential upon the substrate,  
12 wherein the multi-step direct current waveform potential comprises a stepped changing  
13 current density.

1 20. The method of plating according to claim 19, wherein impressing a multi-step  
2 direct-current waveform potential upon the substrate further comprises:  
3 applying a direct-current waveform potential upon the aqueous electroplating  
4 composition before contacting the substrate therewith.

1 21. The method of plating according to claim 19, wherein the method further  
2 comprises:  
3 pre-treating the substrate with a composition selected from deionized water, distilled  
4 water, an acid, a base, a solvent, a reducing agent, and mixtures thereof.

1           22.     The method of plating according to claim 19, wherein the contacting the substrate  
2 comprises rotating the substrate relative to the plating composition at a rate in a range from about  
3 0 to about 500 rpm.

1           23.     The method of plating according to claim 19, wherein contacting the substrate  
2 comprises supplying plating composition at a rate from about 3 L/min to about 60 L/min.

1           24.     The method of plating according to claim 19, wherein the plating composition is  
2 maintained in a temperature range from about 7 C to about 35 C.

1           25.     The method of plating according to claim 19, wherein the multi-step direct current  
2 waveform potential comprises a stepped changing current density that comprises:  
3                 a nucleation current density; followed by  
4                 an initiation current density; followed by  
5                 at least one cycle of a fill current density that comprises a first forward pulse  
6 current density and a second reverse pulse current density; and followed by  
7                 a bulk fill current density.

1           26.     The method of plating according to claim 19, wherein the multi-step direct current  
2 waveform potential comprises a stepped increasing current density that comprises:  
3                 a nucleation current density in a range from about 3 mA/cm<sup>2</sup> to about 70 mA/cm<sup>2</sup>.

1           27.     The method of plating according to claim 19, wherein the at least one cycle of a  
2     fill current density that comprises a first forward pulse current density and a second reverse pulse  
3     current density comprises cycles in the range from 1ns to about 1 min.

1           28.     The method of plating according to claim 19, before contacting a substrate with  
2     the plating composition, the method further comprising:  
3                 forming a seed layer comprising copper upon the substrate, wherein forming a  
4     seed layer is selected from physical vapor deposition and chemical vapor deposition.

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1 29. An article comprising:

2 a substrate containing a recess therein, wherein the recess has a characteristic  
3 width in a range from about 0.02 microns to about 100 microns,; and

4 a copper conductor in the recess, wherein the copper conductor has a grain size in  
5 a range from about 5 nm to about 100 nm.

1 30. The contact according to claim 29, wherein the recess has an aspect ratio in a  
2 range from about 1:1 to about 10:1.

1 31. The contact according to claim 29, wherein the grain originates from a <111>  
2 crystal configuration.

1 32. The contact according to claim 29, wherein the grain originates from a <200>  
2 crystal configuration.